(54) Title: CROSSLINKABLE BIOPOLYMER
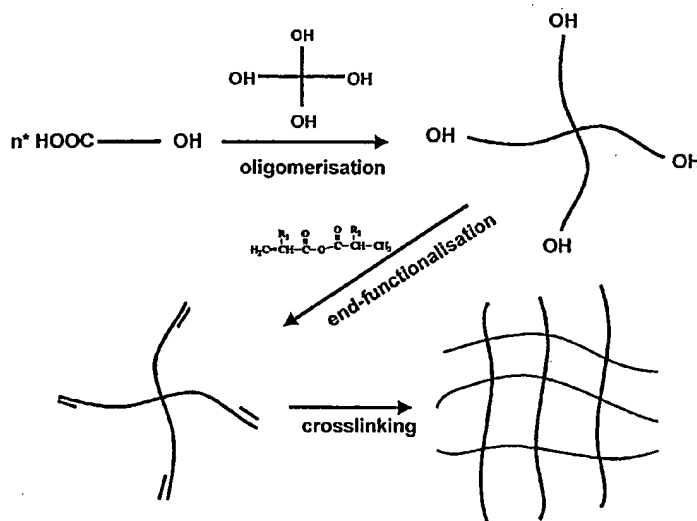
(57) Abstract: The invention discloses composition, prepolymer and method to produce a polymer based on biodegradabler or
essentially renewable crude materials,which can be crosslinked by free radicals. Composition is based on polyesters that are func-
tionalised with unsaturated monomer units, in a way that unsaturated groups can be located along the polymer main chain as well as
at the ends of the prepolymer. In connection to the product production, the prepolymer shall be exposed to free radicals that leads
to network formation. The composition of the crosslinked biopolymer can be adjusted from a stiff engineering material to an elastic
rubbery material. The new biopolymer can be used in composite materials, dispersions, barrier materials, rubbery materials, and in
biomedical applications to mention a few possible application areas.

Crosslinkable biopolymer

The object of this invention is biodegradable crosslinked polymer, which is made from
hydroxy acid or diacids and diols, end-group modifiers, components bringing unsaturated site
to end-groups and possibly components to modify properties, and a method for its
manufacture.

With growing environmental problems the interest in biodegradable and compostable
polymers has increased. Such polymers can be used for example in disposable products,
packages, as paper coatings and to wrap compostable, whereby composting would be an
alternative to recycling or incineration to deal with plastics waste. The high price of
biodegradable plastics limits, however, their use in packages and other bulk applications.

The markets for biodegradable polymers have grown during the last years and they will
expand significantly in the coming years. The reason for growth is partly a growing awareness
on the side of the consumer of the increase in landfill waste due to packaging, and partly the
tightening legislation for recycling, and a concern for a decrease in the non-renewable oil
resources used in the production of traditional polymers. The use of renewable natural
resources is then a significant competitive advantage. Especially the lactic acid used as the
raw-material for the lactic acid polymers is made from renewable natural resources; carbon
source used in the fermentation to lactic acid is starch or sugar, and often the use of by-
products or wastes from agriculture is attempted.

Different coatings are used in huge quantities to coat paper, cardboard, textiles, wood, metals
and polymers. With the coating one strives to improve the product properties of the substrate,
such as barrier properties, for example water or fat retention, and special durability properties,
e.g. water resistance. The coatings usually comprise a viscous three-component system: a film
forming binder, a pigment, and a volatile solvent. These coatings are used either as solutions
or dispersions in the coating applications. The binders in most coatings are either high molar
mass non-reactive organic polymers, or low molar mass reactive polymers, which are further
polymerised.

Biodegradable plastics are usually understood to be polymers that by the influence of microbes or moisture degrade to non-harmful small molecular compounds (mainly carbon dioxide and water). The biopolymers are usually divided into natural and synthetic polymers. To the group of natural polymers belong, *i.a.* proteins and polysaccharides (starch and cellulose based). Synthetic biopolymers are aliphatic polyesters, polyanhydrides, polyorthoesters, water soluble polyvinyl alcohols and some polyurethanes. Biopolymers can also be produced with the help of microbes (*e.g.* polyhydroxy alkanoates). The most important group of biodegradable plastics comprises aliphatic polyesters, the biodegradation of which largely is based on hydrolysable ester bonds.

Among the polyesters one can mention polyglycolide, polylactide, and polycaprolactone and the bacterially made polyhydroxy butyrate and valerate. The polyesters are usually prepeared from hydroxyl acids or diacids and diols. For the aliphatic polyesters to have adequate mechanical properties their molar masses have to be fairly high. The most common means to achieve a high molar mass is to prepare the polyester by a ring-opening polymerisation of lactones.

Lactic acid is one of the potential raw materials for biodegradable commodity polymers. Lactic acid is produced from renewable natural materials (*e.g.* barley, potato, corn/maize) by fermentation. The polymers of lactic acid are thermoplastic, biodegradable polyesters. Poly(lactic acids) (PLA) can be processed with common plastic processing equipment, and they have good mechanical and barrier properties in package applications. PLA is rapidly and completely degraded in composting conditions to biomass, water and carbon dioxide.

The fields of use for polylactides are disposable plates, cups and cutlery, packages for products and technical items, agricultural films and other gardening products, paper and cardboard coating products and products in hygiene and public health. The polymers of lactic acid are also non-toxic, biocompatible materials, and they are used in many applications within orthopaedics, odontology, pharmacy and surgery (*e.g.* bone screws and sutures).

The condensation polymerisation between the hydroxyl and acid groups of lactic acid monomers does not produce polymers of sufficiently high molar mass so that their mechanical properties would be adequate. Consequently, three main routes are used in the

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manufacturing, all of which, however, utilise condensation polymerisation. In the coupling polymerisation method for lactic acid the lactic acid monomers are first polycondensed to low molar mass oligomers, which in the second stage are coupled to each other by the use of different coupling agents, such as di-isocyanates, di-epoxies or bis(2-oxazolines). These

5   coupling methods are described, i.a., in the patent publication US470944. The increasing of the molar mass by increasing coupling reactions demands that the reactive end-groups of the lactic acid oligomers usually are of the same type (either hydroxyl or acid ends). This requirement can be achieved by using long polymerisation times and a low pressure in the condensation reactor, which, however, significantly increases the manufacturing costs. In

10   addition the amount of the by-product, lactide, increases and the yield of the lactic acid oligomer decreases when the polymerisation time is increased.

In the mostly used method cyclic dimers of lactic acid, lactides, are prepared from the oligomers, and they are polymerised to polylactide by ring-opening polymerisation.

15   Production of polylactide by the ring-opening mechanism via the lactide phase yields a high molar mass polymer, but it requires many steps and extremely pure starting materials. Since Carothers presented this polymerisation method in 1932 several papers have been published describing how to improve the polylactide process: (a) Methods for making pre-polymers required for manufacture of lactide are presented, e.g., in US patent publication US5357034;

20   (b) production of crude lactide is shown, i.a., in US5357035; (c) purification of crude lactide to lactide in the patent publication WO9631506; (d) several types of polymerisation methods to polymerise lactide to polylactide are known, for example the one presented in the patent publication FI970651; and (e) removal of residual monomer from polylactide is described in the publication FI970649. In addition, the high temperatures required for processing of

25   thermoplastic polylactide demand (f) thermal stabilisation, which has been described in, i.a., US5338822. However, these several steps (a-f) in the production of polylactide and their sub-processes require many different, often complicated and expensive process equipment, and the total yield of final polylactide from lactic acid often tends to be relatively low, too.

30   In addition to the above mentioned methods a solvent process based on azeotropic distillation is presented in the US patent publication (US5310865, 1994), in which method lactic acid is polyconsenced directly to poly(lactic acid). Lactic acid is polymerised in the presence of a catalyst in some organic solvent, such as anisole or diphenyl ether. The organic solvent forms

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with water an azeotropic mix, by which water can be removed from the reaction mixture, and thus the polycondensation equilibrium is pushed towards the polyester.

In optimised conditions high (upto 300 000 g/mol) molar masses have been achieved. In the
5   mentioned process solvents are used, however, the use of which, and their purification to the required level, and the separation of the final product from the solvents are economically unfavourable. Additionally relatively high catalyst concentrations have to be used in the process.

10   In addition to the above described manufacturing methods for thermoplastic biopolymers, thermoset biodegradable polymers can be made. In the patent publication US4502976 is described the manufacture of a bioerodible water soluble hydrogel by condensation of an unsaturated aliphatic or cyclo-aliphatic dicarboxylic acid or diol, a water soluble polyglycol and a dicarboxylic acid. The aim in the invention is for a medical hydrogel, which type of
15   polymer is not suitable as a coating or barrier material because of its water solubility. In the US publication US4843112 a crosslinkable biodegradable bone cement is presented, a blend of poly(propylene glycol fumarate), ceramics and salts, manufacturing method by condensation and crosslinking with methyl methacrylate.

20   In addition, the patent publication US4888413 presents for medical purposes a poly(propylene glycol fumarate) with a molar mass of 500-3000 g/mol, whereas the EP patent publication EP812868A1 presents a crosslinked polyester based on an unsaturated multi-functional acid (poly(glycol fumarate)) with a molar mass of more than 15 000 g/mol. Several other publications describe methods in which compounds with double bonds are linked to known
25   biodegradable polymers by addition, after which they are crosslinked; for instance maleic acid anhydride has been linked to the hydroxyl end-groups of polycaprolactone. The weakness of these methods is the steps in the ring-opening polymerisation process and further the high demand of conversion on the following addition reaction, which add to the manufacturing costs. In the methods described above it has mainly been the aim to get medical materials
30   compatible with the human organism and priority has not been on the price of the raw-materials for the polymers, complicated reaction systems nor on their biotechnical means of production. Furthermore, the patents described are not based on such biopolymers, which compose of prepolymers produced by polycondensation and thereafter end-functionalised

prepolymers, and which then in the second stage can be crosslinked, thus they do not correspond to the chemical composition in the method and the properties generated equivalent to the present invention. In addition, furthermore the polyesterification reaction is often performed in an organic solvent, which adds to the costs of a high volume production. The weakness of the said materials for industrial high volume production, such as polymer production for making coatings and objects, is thus that they are not applicable due to their chemical composition, high costs of raw-materials, complicated production processes and their material properties.

Finnish patent application 20011999 describes composition and manufacturing method for biopolymer, which is essentially based on hydroxy acids and is crosslinkable by its double bonded monomer units copolymerized into the polymer structure during condensation stage. Such crosslinked polymer, however, has plenty of –OH and possible –COOH end-groups left which results the water sensitivity and hydrophilicity of the polymer. Furthermore, the crosslinking degrees often remain lower than is needed in perspective of obtaining high mechanical toughness properties.

To this level of technique, is surprisingly done an invention, where the crosslinking can be essentially improved by treating the prepolymer end-groups, partly or entirely, with units containing double bonds. Alternatively, the end-groups can be treated with end-blockers containing saturated chain. Attainable advantage of the present invention method compared to presented composition and method in Fl 20011999 is better crosslinking and reduction or removal of free hydrophilic end-groups. Due to these remarks, significant advantage is surprisingly achieved in curing speed, mechanical properties, temperature resistance, strain resistance, water resistance and hydrophilicity and resistance to hydrolysis as well the grease resistance. Highly noteworthy invention concomitant to the method is that composition according to the invention is possible to manufacture even without the use of reduced pressure, which enables very easy and advantageous technical production method carried out in one reactor. Typical composition and chemical structure according to the invention is presented in the figure 1, not however excluding other structures based on the invention.

The purpose of the present invention is to make from lactic acid a new type of a biodegradable crosslinked polymer, which differs essentially by its material composition, its

manufacture and use from earlier presented inventions. One of the aims of the invention is also to produce the mentioned product by a method which is simpler than previous ones.

A furthermore an objective is to eliminate typical drawbacks of lactic acid polymers, essentially the unsatisfactory heat tolerance and brittleness of the materials.

The purpose is that in the manufacture of the polyester, starting materials which are mainly or at least remarkably based on renewable raw materials can be used.

An additional objective is that no by-products such as lactide are removed in the polycondensation reaction from the reaction vessel, thus improving the yield of the product. Furthermore the objective is that the product generated in the polyesterification has not to be purified from monomer residues or other impurities.

A further aim is, that by mixing into the polyester resin a reactive macromonomer it is possible to even more improve the properties of the product and its usability. Now it has surprisingly been observed that these objects are fulfilled by the crosslinked polymer of the present invention as prepared by the methods described herein.

The polymer resin according to the invention is manufactured by condensation polymerisation of a hydroxy acid, such as lactic acid. In the polymerisation is further used itaconic acid or itaconic anhydride, di- or polyfunctional alcohol. It is also possible to use other comonomers in the polycondensation if different properties are desired for the product, such as elasticity. It is possible to add, before the application, a reactive macromonomer to the prepared and still reactive low molar mass polyester resin. In the application to the substrate typical polymer coating and dispersion coating techniques may be used, such as engraved roll coating, spray coating or a layer formation by use of a set of rolls. Crosslinking of the resin to a high molar mass crosslinked polymer takes place by heat, radical producing compounds, UV or VIS light or other radical exposure.

By using the biodegradable thermoset plastic being the object of this invention it is believed that wider operating temperature ranges and improved penetration properties can be achieved compared to thermoplastic biopolymer coatings. It is also possible to tailor the mechanical properties of the end-products from hard to elastic.

The polymer resin according to this invention can be cured and processed by using traditional processing methods for thermoset plastics. Processing at normal pressure include hand laying, spraying, continuous lamination, casting, rotational moulding and making of pipes and containers using a rotating mould. Methods based on compression are compression and transfer moulding (RTM), 10 injection moulding (RIM) and pultrusion. Particularly economical processing method is deep drawing and thermoforming.

The new polymers have a wide field of applications. The polymer can be used as a coating on packages, sacks, bags and films, made of paper, cardboard, cellulose, starches and recycled fibres. Formed pieces moulded according to methods mentioned above as well as heat and blow moulded packages, sacks, bags and bottles can be produced from them. Furthermore, they can be used in the manufacture of expanded plastics products, cellular plastics and foams that can be used as cushioning in packages. One advantageous application field according to the invention is different types of composite materials, where filler or reinforcement components are combined with the polymer according to the invention. Advantageous fields of applications to mention are also layered boards, particle boards and similar products, veneers, hardboards and impregnated papers. Also, an advantageous field of application is manufacture of composite materials and structures based on the biopolymer. Particularly one object to mention is the possibility to produce plastic processing to materials based on paper boards or papers or cellulose fiber materials. From the polymer resin according to this invention can be prepared dispersions and emulsions which can further coat paper or paper board or other materials or they can be used as glues. The list described above contains some typical fields of applications, however, not outlining other possible applications of the invention. Crosslinkable polymer according to the invention can be advantageously used as glue, binder or barrier layer.

They are also applicable as coatings or matrices for controlled release fertilisers, plant protection agents, insecticides and pharmaceutics. Furthermore, one advantageous field of application for materials according to the invention are pharmaceutical applications and surgery, where particularly biocompatibility and biodegradation are advantages in the applications of tissue engineering and controlled active agent and drug release. In the applications of tissue engineering to the polymer according to the invention can be blended components increasing the bioactivity such as bioactive glass or hydroxy apatite or other

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active substances or drugs or biologically active components and further, porosity can be produced to the polymer with several different techniques.

The invention is based on the idea that the polyester resin is hardened to a solid, thermoset type material by a crosslinking or curing reaction. Additionally the option prevails to add in

5   the preparation stage to the reaction mixture a monomer containing a flexible main chain, such as an ε-caprolactone comonomer. The object of the caprolactone units is to induce flexibility to the material, to decrease the glass transition temperature, and, by decreasing the melt viscosity, to act as an internal plasticiser. Caprolactone is an advantageous comonomer in the sense that it is biodegradable, and thus the biodegradablity of the end-product is

10   maintained.

The process according to the invention is basically a two stage one, where the first stage comprises polymerisation of the resin, in which from lactic acid and possible not compulsory from comonomer such as itaconic acid either a linear or star shaped polyester with a desired molar mass can be made in a reasonable time, keeping formation of side products low. The di-

15   or multifunctional alcohol has an important role in tailoring the molar mass and molecular structure. Selection of alcohol component can influence the rigidity of chain, glass transition temperature and hydrophilicity and by that the water retention.

Special example of method according to the invention is to use betulin as difunctional alcohol. Betulin also known as betulinol, which occurs abundantly in the bark of birch, is

20   biomass based bulky steroid type of diol, which also has a double bond. Now it is surprisingly observed to be useful in the polymer structure according to the invention.

Central parameters in the method are the monomer ratios, the polymerisation temperatures, the temperature increase profile, the methods to remove the condensation water, the

25   comonomers and the catalysts.

Further essential improvement according to this invention to the previous level of technique is that the linear of branched prepolymer manufactured by direct polycondensation can be end-functionalised during the condensation reaction or in the end of it in a separate reaction so that

end-groups of prepolymers are not any longer –OH or –COOH functional groups. Hydroxyl end-groups can be converted for example by treatment with a dianhydride to unsaturated reactive double bonds. Typically, however not outlining the applicability of technique can be mentioned a dimethacrylic anhydride as advantagenous end-group modifier. Attainable advantage is then that the crosslinking of polyester polymer manufactured by direct condensation improves. In other words, its crosslinking speed increases and crosslinking degree increases which have huge significance considering industrial production processes and mechanical strength abilities of end-products, such as tensile strength, impact strength, creep resistance and high temperature resistance just to mention a few. Furthermore, according to the invention, by end-functionalisation and changing the character of the prepolymer it is surprisingly observed that is possible to influence favourably the reduction of the water and grease absorbance of both the prepolymer and crosslinked end-products which facts are important among others in both technical and package applications. In consequence, surprisingly prepolymer without end-group modification when immersed in water absorbs water already in few hours changing simultaneously to soft toffee-like mass. While, a composition according to the invention is completely water proof when its end-groups have been treated with a method according to the invention. Similarly, grease absorption character is extremely low. Same consequence is achieved when end-functionalised prepolymer is crosslinked. This characteristic have crucially important technical significance considering the applicability of directly polycondensated poly(lactic acid) as technical material. One advantageous new possibility for such a material opens in the production of dispersions and emulsions, where water is the medium substrate and therefore a good resistance of water is needed already in the prepolymer stage.

Furthermore, it has been surprisingly noted, that treatment of end-groups can be also done, partly or entirely, by saturated components while affecting only on the hydrophilic character but not adding up the crosslinking. In this case, the treatment of end-groups can be done with compounds for example acetic acid, other organic acids and their different anhydrides, fatty acids such as pine oil, castor oil and linoleic acid to mention a few.

Furthermore, it is also possible to perform the treatment of end-groups with isocyanates or in the case of –COOH end-groups also with alcohols or epoxy compounds.

In the second stage of the method a crosslinked polyester with a high molar mass is formed by crosslinking the resin, using a radical forming compound such as a peroxide. Initiation of the reaction is achieved by heat, light, by radiation or by redox-initiation. Central elements at this stage are the mixing temperature, crosslinking temperature, uv curing parameters, used

5   crosslinking agents and their amount, accelerators, inhibitors and the technical solutions (heat, light and their combinations) of crosslinking.

When needed, it is possible to add to the prepared reactive polyester resin a reactive macromonomer before the cross linking of the second stage of the process. As defined in the

10   invention, the reactive macromonomer can be a small molar mass polymer made from a hydroxy acid and possibly other comonomers, itaconic acid and a polyol. By its use application can be eased by reducing the melt viscosity, the level of crosslinking and the crosslink density can be influenced, and it can bring flexibility to the material.

15   The invention will be more closely looked at below with a detailed description and corresponding examples.

The first stage of the method according to the present invention comprises the condensation polymerisation of the resin. In the polymerisation a polyester with a desired molar mass is

20   prepared from (i) a hydroxy acid or a diacid and a diol, (ii) a functionalising agent which can be a diol or polyfunctional alcohol, or a dicarboxylic acid or polyfunctional carboxylic acid, and (iii) possibly other monomers such as ε-caprolactone, unsaturated components such as itaconic acid or other unsaturated difunctional monomers.

25   The hydroxy acid monomers used in the invention to prepare the resin are typically comprises α-hydroxy acids, β-hydroxy acids or lactones. It is especially advantageous to use aliphatic or aromatic a-hydroxy acid monomers, such as L-lactic acid or D-lactic acid or their mixtures (so called racemic D,L-lactic acid), glycolic acid, 6-caproic acid, L- or D- mandelic acid, L-lactide or D,L-lactide. The hydroxy acid monomers can also be multifunctional. Malic acid

30   and citric acid can be mentioned as examples.

The unsaturated difunctional monomers used in the invention typically comprise unsaturated difunctional acids, such as itaconic acid, itaconic acid anhydride, maleic acid, maleic acid

anhydride or fumaric acid, or unsaturated difunctional alcohols, such as 1,4-butenediol, 1-propene-1,2-diol, 2-heptene-1,7 -diol, 3-heptene-1,7 -diol, 2-hexane-1,6-diol, 3-hexane-1,6-diol, 1-pentene-1,5-diol or 2-pentene-1,5-diol or betulin alias betulinol.

Especially interesting is such an application of the invention in which the hydroxy acid and the unsaturated difunctional monomer are based on renewable raw materials and can be manufactured by biotechnical methods, such as L-lactic acid and itaconic acid.

The number of reactive groups and the amount of the functionalising agent used in the manufacture of the resin determine the molecular structure (e.g. linear or star shaped) and the molecule size (molar mass) of the resin formed in the polymerization. The functionalising agent to be used is typically a polyfunctional alcohol, such as butanediol, glycol, propanediol, hexanediol, penta-erythritol, mannitol, glycerol or different polyglycerols, or a multifunctional acid, such as 1,1,3-propane tricarboxylic acid, 1,1,2-ethane carboxylic acid or 1,2,3,4-cyclo-pentane tetracarboxylic acid or betulin alias betulinol.

Depending on the amount of starting materials the composition of the polyester resin is typically 20-99 mole % lactic acid and 80-1 mole % the functionalising agent and crosslinking agents. When a rubber-like ductility and elasticity is wanted, a desired quantity, typically 1-99 mole %, of a cyclic aliphatic lactone, e.g. ε-caprolactone, can be added into the mixture of hydroxy acid monomers. Correspondingly, when stiffness and high operating temperatures are wanted, mandelic acid can be added. The above percentage amounts are calculated on the total monomer quantity. Resins with star shaped structures can be prepared by using polyfunctional alcohols, such as pentaerythritol. Copolymerisation of pentaerythritol (PE), lactic acid (LA) and itaconic acid (IT) by a condensation reaction yields a polyester resin, which comprises the following construction units, however not excluding other possible structures:
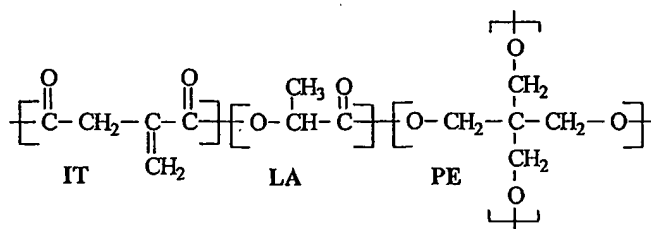
Elastic resins of star shaped structure can be prepared by copolymerisation of multifunctional alcohols, such as pentaerythritol (PE), lactic acid (LA), itaconic acid (IT) and ε-caprolactone (CL) by a condensation reaction. A polyester resin composed of the following construction units is then achieved, however not excluding other possible structures:
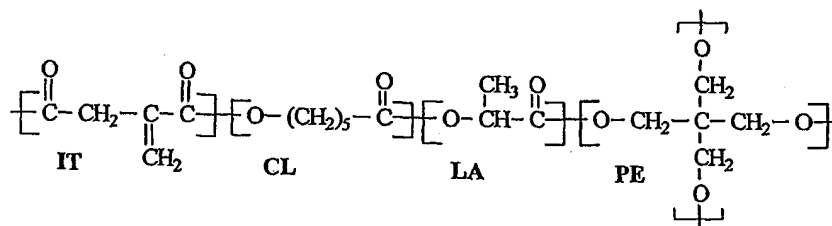
The properties of the resin can be adjusted by changing the ratios of the monomers used. The molar mass can be adjusted by changing the pentaerythritol-lactic acid ratio, and the crosslink density can be adjusted by changing the lactic acid-itaconic acid ratio. Additionally, also the elasticity of the resin, its degree of rubbery properties, can be adjusted by changing the resin composition, i.e. altering the amount of caprolactone.

Structurally linear crosslinkable resins can be prepared by using difunctional alcohols, such as 1,4-butanediol (BD). Copolymerising it with lactic acid (LA) and itaconic acid (IT) in a condensation reaction yields a polyester resin, which comprises the following structural elements, however not excluding other possible structures:
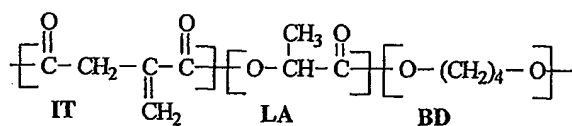
Advantageous crosslinking structures are achieved when polymerization is performed in two stages: In the first stage, the polycondensation is performed, and in the second stage, the end-groups are, partly or entirely, treated by unsaturated compound for example profitably with methacrylic anhydride, when for example the following structural elements are attained, however not excluding other possible ways to modify end-groups:

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$$CH_2=\overset{\underset{\displaystyle CH_3}{|}}{C}-\overset{\underset{\displaystyle O}{||}}{C}\underset{LA}{\left[O-\overset{\underset{\displaystyle CH_3}{|}}{CH}-\overset{\underset{\displaystyle O}{||}}{C}\right]}\underset{PE}{O-CH_2-\overset{\underset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-CH_2-O-}$$

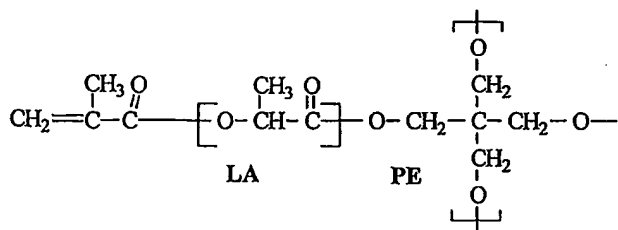As above, the properties of the resin can be adjusted by changing the ratios of the monomers

5   used. The molar mass can be tailored by changing the butanediol-lactic acid ratio, and the crosslink density can be adjusted by altering the lactic acid-itaconic acid ratio. Further, part of the lactic acid can be replaced with caprolactone, whereby the elasticity of the resin will increase. The polycondensation of lactic acid is an equilibrium reaction. In order for the polymerisation to proceed, the reaction equilibrium should be pushed to the side of the

10   products. To move the equilibrium to the right, especially at the end of the reaction, is usually difficult, because the condensation water escapes extremely slowly when the viscosity of the reaction mixture increases. Shifting of the equilibrium is achieved by reducing the pressure, increasing the temperature and by the use of catalysts. When the polymerisation temperature exceeds 210 °C, the breakdown of the polymer chains starts to limit the polymerisation rate.

15   In addition, the molar mass of the poly(lactic acid) is decreased by depolymerisation, by which the harmful side-product lactide is formed, and its formation increases also substantially at temperatures above 220 °C. Poly(lactic acid) with a high molar mass is very cumbersome to prepare by polycondensation without solvents, special catalysts and long polymerisation times. The reaction is also very sensitive to monofunctional impurities, which

20   can act as chain terminators. Thus condensation polymerisation of lactic acid is usually limited to preparing polymers of low molar mass, typically 5000-20000 g/mole, (also called lactic acid oligomers). The number average molar mass of polyesters should be at least 25 000-40 000g/mole for the product to have useful physical properties.

25   Remarkable invention concomitant to the method is, that surprisingly, compositions according to the invention are possible to manufacture even without any reduced pressure which enables highly easy and advantageous technical manufacture. This kind of manufacture is possible, because the crosslinking prepolymer does not always need to be in a high molar mass level, at which an application along with the method is possible, where reduced pressure is not used or

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only used slightly in the condensation reaction. In addition to its economical and technical simplicity, this method has an advantage that the vaporisation of the low molecular components is not so drastic, for example, the formation of lactide is minor in the case of lactic acid condensation.

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The advantages of the present invention can be regarded to be that high molar masses in polymerising the resin are not strived at. Typically, the molar masses are between 500 and 10000 g/mole. Further, because the subreactions are based on reaction of the double bonds and not on subreaction of free end-groups, it is considered that bringing the reactions of the end-groups of the monomers in the reaction mixture to an end is not critical for this process. Hereby substantial process technical advantages are achieved, such as shorter polymerisation times, lower polymerisation temperatures, and easier low pressure conditions. An advantage of the invention is also that no solvents are needed in the polymerisation. Further, according to the method for manufacture in the invention it is possible to decrease formation of the side product, lactide, due to the monomer composition and lower polymerisation temperatures. Further, because the crosslinking reaction and the crosslink density depend primarily on opening of the double bonds, and not on the molar mass of the prepolymer, or on defined exact stoichiometric ratios between end-groups, the method gives the possibility to use also "food grade" or less refined and purified lactic acid.

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The polycondensation reaction is autocatalysed by the acid groups in the monomers. When the reaction proceeds the concentration of acid groups decreases, however, and the reaction slows down. To avoid this it is recommended to use a catalyst in the polyesterification, usually 0.1 ...0.5 weight %. In the polycondensation of lactic acid, for instance protonic acids, Lewis acids, organometallic compounds, metal oxides and metal salts of titanium, tin, zirconium and lead can be used as catalysts.

During the polycondensation it is important to make sure that the double bonds do not polymerise with each other by a chain polymerisation and thus prematurely crosslink the polymer. Inhibitors added to the reaction mixture react with radicals to form inactive molecules. Thus a premature curing of the resin during the polycondensation reaction is blocked, and also the work time during application is prolonged. Due to the inhibitors it is further possible to extend the storage time of the polyester resins by several months or even

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years. Most commonly used inhibitors are quinones (e.g. p-benzoquinone, hydroquinone and 1,4-naphthoquinone), aromatic nitro-compounds (tri-nitrobenzene), sulphur, metal halides and copper compounds. Especially good inhibitors are such compounds that do not contain hydroxyl groups that might react with the monomers of the reaction mixture. Such are p-

5   benzoquinone, 1,4-naphthoquinone and 2,5-diphenyl-p-benzoquinone. The amount of inhibitors is typically 0.01 ...0.1 weight % of the resin.

When condensation proceeds to the desired level an –OH end-functionalised prepolymer is typically formed (or in the alternative procedure –COOH end-functionalised). These –OH

10   groups can be converted, partly or entirely, to reactive double bonds by adding unsaturated acid, acid anhydride, acid chloride, isocyanate compound, alcohol or epoxy compound to the reactor. By using acid anhydride typical reaction time is 3 hours at temperature of 160°C, when anhydride is added directly to the condensation reactor. Treatment provides reactive oligomer with significant amount of double bonded end-groups.

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Production of the resin, or the condensation polymerisation of lactic acid, can be made in any equipment that is fit for esterification reactions. According to one preferable alternative the polyesterification is carried out as a bulk polymerisation in the melt, whereby water formed as a condensation product can be removed by leading a dry inert gas into the polymer melt with

20   simultaneous mixing. Abstraction of water can also be improved by using vacuum, whereby the pressure is decreased step-wise. According to one favourable alternative the polyesterification is started at a temperature of about 90 °C, which is gradually increased to 180 °C. The pressure is correspondingly decreased step-wise between 500 and 30 mbar, and the condensation water is continuously removed by nitrogen. At the end of the

25   polyesterification the fraction with a low molar mass can be removed, if desired, from the reaction mixture by decreasing the pressure further, whereby the aforementioned fraction is distilled off.

The polyesterification is preferably performed in the presence of a catalyst, whereby

30   according to one preferable embodiment the catalysts used are typical polyesterification catalysts. Such catalysts are, e.g., salts, or alkyl or alkoxy compounds of aluminium, iron, tin, titanium or zinc.

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A polyester resin prepared in the way as described above can further be blended with well-known fillers, reinforcements and thixotropic materials. Typical fillers and reinforcing agents are talcum, wollastonite, chalk, glass, bioactive glass, hydroxy apatite, quartz and silicates, wood flour, jute, hemp, cellulose, starch, cotton, flax, graphite, aluminium hydroxide, carbon

5   black and different pigments such as titanium dioxide. Further, to a polymer according to the invention can be blended bioactive glass, hydroxyl apatite, carbon nanofibers, nanoclays such as montmorillonite or microsilica.

The polyester resins flow rather easily especially on vertical surfaces if they do not have

10 thixotropic properties. The most common agent giving thixotrophy is a specially made silicon dioxide. Its effect is based on hydrogen bridges between the hydroxyl groups of silicon dioxide and the polyester molecules. These hydrogen bridges increase the viscosity of the resin when the resin is not handled, and thus the flowing is decreasing. Thixotropic additives make the cured resin slightly opaque.

15

Crosslinking of a low molar mass resin to a high molar mass polymer changes, and usually improves, its physical properties compared to the uncured resin. Especially the temperature range of the polymer is widened, and the barrier properties are improved. The improved properties are especially seen above theglass transition temperature. Crosslinking of the resin

20 as described in the invention can be performed by forming from the resin a polymer film by any known film formation method and equipment, which is suitable for making a polymer film (extrusion, dispersion, spray coating), or by making a formed object using the earlier · mentioned traditional processing methods for thermoset resins, such as compression and transfer moulding, RIM injection moulding and pultrusion. Alternatively a film can be made

25 on the surface of the material to be coated, such as paper, cardboard, wood, polymer, glass, metal or other material, by any known film formation method and equipment, which is suitable for making a polymer film on the surface of a material (extrusion, dispersion, spray coating). The resin may be cured by heat, light, by radiation or a combination of these in an apparatus adapted for this. The curing can take place immediately after film formation before

30 application, or after application.

In the curing method described in the invention, the reaction of the double bonds of the resin, or the crosslinking, is initiated by producing radicals in the resin using different radical

17

forming compounds for example organic peroxy compounds, such as diazyl peroxides, peroxy esters, peroxy dicarbonates, monoperoxy carbonates, diperoxy ketals, dialkyl peroxides, sulfonyl peroxides, ketone peroxides, and, peroxy carboxylic acids. Examples could be dibenzoyl peroxide, di(2,4-dichlorobenzoyl)peroxide, di-t-butyl peroxide, diacetyl

5   peroxide, dilauroyl peroxide, didekanoyl peroxide, di-isononanoyl peroxide, succinic acid peroxide, acetyl cyclohexanesulfonyl peroxide, m-chloroperbenzoic acid, tert-butyl perbenzoate, tert-amylperbenzoic acid, and tert-butylperoxy maleic acid. Further inorganic peroxides can be used, e.g. hydrogen peroxide, oxygen, ozone, azo compounds, redox initiators, light initiators, polymeric peroxides, and other means to produce radicals and

10   combinations of these.

In the curing method of this invention curing temperatures that can be used may be ambient or higher depending on the mechanisms of radical formation.


15   By the embodiment of this invention the curing of the resin can be speeded up and the curing temperature be decreased by adding accelerators before curing of the resin. Accelerators that can be used are, e.g., metal compounds, such as cobalt compounds, organic amines or other known accelerators. Accelerators, such as cobalt octoate and naphthenate, and amine accelerators can be used dissolved either in a suitable plasticiser or solvent or as such. A

20   typical dosing is 0.015 ...0.06 weight % cobalt or other metal, and 0.1 ...0.4 weight % amine, depending on the degree of acceleration and the resin quality.

By the embodiment of the invention the reactions of the double bonds of the resin, or crosslinking sensitivity and rate, can be adjusted by the use of inhibitors already in the

25   condensation polymerisation, or these can be added to the resin after the condensation polymerisation The inhibitors react with the radicals forming inactive molecules. By this premature curing of the resin is hindered and the working time is prolonged. After the inhibitors are exhausted (or reacted with the radicals) polymerisation and curing of the resin commences.

30

By the embodiment of the present invention, in the manufacture of the crosslinked biodegradable polymer coating the polymer resin can be cured by letting its double bonds react with each other, that is by homopolymerisation, as described above or alternatively

18

possible mechanism is based on a reaction of double bond with hydrogen from the polymer chain and formation of new carbon-carbon bond. Additionally, curing can be achieved also by using a reactive macromonomer together with the polymer resin, whereby the double bonds of the different compounds react with each other forming a crosslinked polymer with a

5   network structure. By using a reactive monomer, or reactive macromonomer, together with the polymer resin as according to the method, of this invention, the crosslink density can be affected and elastic, rubber like materials can be achieved, and the viscosity of the resin can be reduced.

10   In the embodiment of the invention rather low molar mass unsaturated polyester resins can be used as reactive macromonomers. These elastic resins of linear structure can be prepared by copolymerising difunctional alcohols, such as butanediol (BD), lactic acid (LA), itaconic acid (IT) and f.-caprolactone (CL) in a condensation reaction. Thereby a polyester resin is achieved, which is composed of the following structural units, however, not excluding other

15   possible structures:
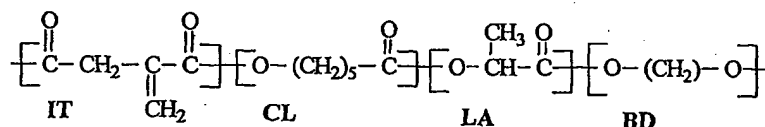
The present invention is described in more detail by the following examples.

20

Example 1.

Preparation of a star shaped poly(lactic acid-itaconic acid) resin

Into a 2 litre Rotavapor equipment, used as the reactor, 437.5 g of L-lactic acid was added

25   (88% water solution corresponding to 89 mole-%), 47.9 g of itaconic acid (9 mole-%), 14.5 g of pentaerythritol (2 mole-%) and 0.19 g of tin(II) octoate. Dry nitrogen was led into the reactor and a 500 mbar absolute pressure was established. The reactor vessel was partly immersed in an oil bath with a temperature of 90 °C. The temperature of the oil bath was increased at a rate of 30 °C /h to 120 °C, and the reaction mixture was mixed by starting the

30   rotation at a speed of 100 rpm. The temperature of the oil bath was evenly increased by 15 °C/h until 180 °C, where it was kept until the end of the polymerisation. The pressure was

decreased every hour by the following steps: 500 (start) -500- 450- 400 -350- 290- 190- 140-
90- 60- 50- 40 -30 mbar, at which pressure it was kept to the end of the polymerisation.
Bubbling of nitrogen was continued throughout the polymerisation and the formed water was
collected as it evolved. Total polymerisation time was 24 hours.

5

During the polymerisation no lactide was formed on the reactor walls, condenser or receiver,
although lactide typically forms in a condensation polymerisation of lactic acid. The molar
mass of the obtained polymer was analysed with a SEC equipment (Size Exclusion
Chromatography), and the number average molar mass (M_n was measured as 1500 g/mole,

10   and the weight average molar mass (M_w) as 3900 g/mole, compared with polystyrene
standards, and thus the molar mass distribution was 2.6. DSC analysis (Differential Scanning
Calorimetry) revealed, that the glass transition temperature of the polymer was 33 °C, and no
melting peak of crystals was observed, so the polymer was completely amorphous. By using
FTIR (Fourier Transform Infrared Spectroscopy), characteristic peaks of both double bonds

15   (1640 cm^{-1}) and ester bonds (1750 cm^{-1}) were seen in the polyester resin.

Example 2.
Preparation of a star shaped poly(lactic acid-itaconic acid-ε-caprolactone) resin

20   The polymerisation was performed like in Example 1, but the amounts of the ingredients were
846.3 g of aqueous L-Iactic acid (86 mole-%), 66.2 g of itaconic acid (6 mole-%), 67.4 g of ε-
caprolactone (6 mole-%), 20.1 g of pentaerythritol (2 mole-%) and 0.39 g of tin(II) octoate,
and the polymerisation time was 26 hours.

25   The M_n value of the obtained polymer was 2300 g/mole, measured with the SEC equipment,
and its M_w value 7100 g/mole compared to polystyrene standards, and thus the molar mass
distribution was 3.1. DSC analysis revealed that the glass transition temperature of the
polymer was 26 °C, and no melting peak was observed. By using FTIR (Fourier Transform
Infrared Spectroscopy) peaks characteristic of both double bonds (1640 cm^{-1}) and ester bonds

30   (1750 cm^{-1}) were observed in the polyester resin.

Example 3.
Preparation of a star shaped poly(lactic acid-itaconic acid-ε-caprolactone) resin

The polymerisation was performed like in Example 1, but the amounts of the ingredients were 794.7 g of aqueous L-lactic acid (81 mole-%), 72.5 g of itaconic acid (7 mole-%), 110.7 g of ε-caprolactone (10 mole-%), 22.0 g of pentaerythritol (2 mole-%) and 0.39 g of tin(II)

5   octoate, and the polymerisation time was 26 hours.

The M_n value of the obtained polymer was 2800 g/mole, measured with the SEC equipment, and its M_w value 7600 g/mole compared to polystyrene standards, and thus the molar mass distribution was 2.7. DSC analysis revealed that the glass transition temperature of the

10   polymer was 18 °C, and no melting peak was observed. By using FTIR (Fourier Transform Infrared Spectroscopy) peaks characteristic of both double bonds (1640 cm^{-1}) and ester bonds (1750 cm^{-1}) were observed in the polyester resin.

        Example 4.

15   Preparation of a linear poly(lactic acid-itaconic acid) resin

The polymerisation was performed as in Example 1, but the amounts of ingredients were 401.0 g of aqueous lactic acid (82 mole-%), 54.9 g of itaconic acid (9 mole-%), 44.1 g of 1,4-butanediol (9 mole-%) and 0.22 g of tin(II) octoate, and the polymerisation time was 27

20   hours.

The M_n value of the obtained polymer was 2100 g/mole, measured with the SEC equipment, and its M_w value 4100 g/mole compared to polystyrene standards, and thus the molar mass distribution was 1.9. DSC analysis revealed that the glass transition temperature of the

25   polymer was 9 °C, and no melting peak was seen. By using FTIR (Fourier Transform Infrared Spectroscopy) peaks characteristic of both double bonds (1640 cm^{-1}) and ester bonds (1750 cm^{-1}) were observed in the polyester resin.

        Example 5.

        Preparation of a reactive macromonomer

30

The polymerisation was performed as in Example 1, but the amounts of the ingredients were 55.7 g of aqueous L-lactic acid (13 mole-%), 121.9 g of itaconic acid (25 mole-%), 248.3 g of

ε-caprolactone (50 mole-%), 74.1 g of 1,4-butanediol (13 mole-%) and 0.18 g of tin(II) octoate, the polymerisation time being 26 hours.

Using the SEC apparatus it was determined that the M_n value of the obtained polymer was
5   3000 g/mole and the M_w value 9200 g/mole, compared to polystyrene standards, and thus the molar mass distribution was 3.1. DSC analysis gave a glass transition temperature of -49 °C, and no melting peak was observed.

Example 6.
10   Crosslinking of a poly(lactic acid-itaconic acid) resin using a reactive macromonomer

To the polyester resin according to Example 1, an amount of 20 weight % of the macromonomer according to Example 5 was blended in a melting mixer at a temperature of 90 °C for two minutes, after which 2 weight % di-tert-butylperoxide (Trigonox B) was added.
15   After two minutes of mixing 1 mm thick films were compression moulded at 175 °C. The films were cured in a heating chamber at a temperature of 125 °C for 1,2 and 4 days, whereby a degree of crosslinking of 89% (1 day), 86% (2 days), and 91 % (4 days) were obtained. The glass transition temperatures of these crosslinked polymers were 33 °C, 39 °C and 42 °C, respectively.
20

Example 7.
Crosslinking of a poly(lactic acid-itaconic acid) resin using a reactive macromonomer

To the polyester resin according to Example 1 (80 weight %) the macromonomer according
25   to Example 5 (20 weight %) was blended in a melting mixer at a temperature of 90 °C for two minutes, after which 2 weight % di-tert-butylperoxide (Trigonox B) was added. After two minutes of mixing a 1 mm thick film was compression moulded at 175 °C. The films were cured at a temperature of 175 °C for 12 minutes, yielding a degree of crosslinking of 85 %. The modulus, tensile strength and elongation of the cured film were 31 MPa, 6 MPa and 148
30   %, respectively.

Example 8.

Use of a reactive macromonomer at crosslinking of a poly(lactic acid-itaconic acid) resin cardboard coating

To the polyester 1 (80 weight %) was blended the reactive macromonomer 1 (20 weight %)
in a melting mixer at a temperature of 90 °C for two minutes, after which 2 weight % di-tert-butylperoxide (Trigonox B) was added. After 2 min mixing a cardboard was coated with the polymer and cured in a compression mould at 175 °C for 1, 3, 6 and 12 min. The formed coatings were clear, had a hard surface and were flexible.

Example 9.
Preparation of the itaconic acid containing resin without reduced pressure

Preparation of a star-shaped poly(lactic acid –itaconic acid) resin.Reaction was performed in a 250 ml glass reactor where was added 227.8 g of aqueous L-lactic acid (88% water solution corresponding to 88 mole-%), 27.2 g of itaconic acid (8 mole-%), 13.6 g of pentaerythritol (4 mole-%) and 0.1 g of tin(II) octoate. Into the reaction vessel was led nitrogen and it was immersed partly into the oil bath with temperature of 90°C and the mixing was start at a speed of 200 rpm. The temperature was increased at a rate of 25°C/h to 150°C. The temperature was evenly increased at a rate of 15°C/h to 180 °C, where it was kept during the whole polymerisation. Bubbling of nitrogen was continued throughout the polymerisation and the formed water was collected as it evolved. Total polymerisation time was 11 hours. The product resin was hard, clear but brittle, yellowish in colour and it was observed to crosslink by radicals.

Example 10.
Elastic version of Example 9

Preparation of poly(lactic acid-itaconic acid-ε-caprolactone) resin. Polymerisation was performed as in the Example 10, but the amounts of the ingredients were 113.6 g of aqueous L-lactic acid (71 mole-%), 12.3 g of itaconic acid (6 mole-%), 6.4 g of pentaerythritol (3 mole-%), 35.7 g of ε-caprolactone (20 mole-%) and 0.05 g of tin(II) octoate. Total polymerisation time was 17 hours. The product resin was sticky, elastic, rubbery, yellowish in colour and it was observed to crosslink by radicals.

Example 11.

End-functionalisation

5   Preparation of methacrylated poly(lactic acid-itaconic acid) resin. Reaction was performed in
a 250 ml reaction vessel, whereat was added 128.3 g of the polyester resin according to
Example 9 (80 wt-%) and 25.7 g of methacrylic anhydride (20 wt-%). Nitrogen was led to the
reaction vessel and it was partly immersed in an oil bath with a temperature of 90° C. The
temperature of the reaction mixture was increased to the temperature of 160° C during half an
10   hour and was kept there during 3 hours with mixing speed of 200 rpm. Hard brittle resin was
obtained which was observed to crosslink easily by radical, redox and photo initiators.

Example 12.

Preparation of linear poly(lactic acid-itaconic acid-betulin) resin
15

Polymerisation was performed in the same principle as in Example 9, but the betulin was
added to the reaction mixture in three portions during first two hours. The amounts of the
ingredients were following: 85.2 g of L-lactic acid (89 mole-%), 7.4 g of itaconic acid (5.5
mole-%), 25 g of betulin (5.5 mole-%) and 0.0375 g of tin(II)octoate. Total polymerisation
20   time was 14 hours. The product was hard, brittle, shiny, orange mass, which was water
resistant. Synthesis product was observed to crosslink with end-functionalisation (Example
11) by radicals.

25   Example 13.

Preparation of star-shaped poly(lactic acid-itaconic acid-betulin) resin

Polymerisation was performed as in Example 3, but the amounts of ingredients were
following: 85.2 g of L-lactic acid (78 mole-%), 25.9 g of itaconic acid (16.5 mole-%), 1.4 g of
30   pentaerythritol (0.8 mole-%), 25 g of betulin (4.7 mole-%) and 0.0375g of tin(II)octoate.
Total polymerisation time was 20 hours. As product, was obtained hard bittle browish yellow
mass, which was end-functionalised according to the example 11 and finally crosslinked by
radicals.

24

Example 14.

Preparation of star-shaped poly(lactic acid) resin

5   Polymerisation was performed as in Example 8, but the amounts of ingredients were 227.3 g
of L-lactic acid (99mole-%), 3.1 g of pentaerythritol (1 mole-%) and 0.1 g of tin(II)octoate.
Time of polymerisation was 19 hours. As product, was obtained clear hard and brittle mass,
which as end-functionalised according to Example 11 crosslinked by radicals to hard, and
both water and grease resistant material.

10

Example 15.

Crosslinking a film by heat

To a polyester resin according to Example 8 was blended 2 wt-% of bis(tert-
15   butylperoxyisopropyl)benzene (Perkadox 14) in a melting mixer at a temperature of 80°C.
After two minutes of mixing the blend was compression moulded to 2 mm thick films using
125, 135, 170°C crosslinking temperatures, whereat 30, 35, 45wt-% crosslinking degrees alias
gel contents were obtained, respectively. In all conditions, the obtained products were
crosslinked mechanically hard plactic-like material.

20

Example 16.

Crosslinking using a reactive macromonomer

To a polyester resin according to Example 1 was blended 5 wt-% of 1,4-butanediol-
25   dimethacrylate and 2 wt-% of bis(tert-butylperoxyisopropyl)benzene (Perkadox 14) in a
melting mixer at a temperature of 80°C. After two minutes of mixing the blend was
compression moulded to 2 mm thick films at a temperature of 170°C using times 6, 8, 12 min
whereat 36, 37, 42wt-% crosslinking degrees alias gel contents were obtained.

30   Example 17.

To a polyester resin according to Example 11 was blended 1 wt-% of bis(tert-
butylperoxyisopropyl)benzene (Perkadox 14) in a melting mixer at a temperature of 70°C.

25

After two minutes of mixing the blend was compression moulded to 2 mm thick films at a temperature of 150°C using time of 2 min whereat 85 wt-% crosslinking degree alias gel content was obtained. Crosslinked polymer was clear, smooth at surface and extremely tough, in addition, it was observed to resistant to water and oily compounds.

5

Example 18.

Fiber glass composite

To a polyester resin according to a Example 11 was blended 1 wt-% of bis(tert-
10   butylperoxyisopropyl)benzene (Perkadox 14) in a melting mixer at a temperature of 70°C during 2 minutes. The mixture was impregnated into glass fiber mat by compression mould using processing temperature of 80 °C. The plate was cured at 150°C for 1, 2, 3 minutes. The composite contained 60 wt-% of polyester resin and 40 wt-% of glass fiber. The crosslinked composite was extremely tough and stiff, smooth and clear at the surface.

15

Example 19.

Cotton composite

Composite of polyester resin and cotton was prepared as in Example 18, but the cotton was
20   used instead of the glass fiber. Different composites was prepared by adding the amount of cotton layers, 2-, 3-, 4-, 6-, 8-layered plates, whereat the polyester resin impregnated through the cotton layers entirely. Composite plates were smooth at the surface, and tough and stiff.

Example 20

25   Composite with bioactive glass

To an end-functionalised polyester resin according the Example 11 was blended 20 wt-% of bioactive glass in a melt mixer at the temperature of 70 °C for 1 minute and 1 wt-% of bis(tert-butylperoxyisopropyl)benzene (Perkadox 14) was added and the mixing was
30   continued another 2 minutes. From the mixture was compression moulded 2 mm thick films at 160°C for 1 min whereat an even hard composite plate was obtained which is resistant to water and oily compound.

26

Example 21.

Cellulose fiber composite

To an end-functionalised polyester resin according the Example 11 was blended 1 wt-% of
5   bis(tert-butylperoxyisopropyl)benzene (Perkadox 14) in a melt mixer at the temperature of 70
°C for 2 minute. The mixture was impregnated to hard cellulose board by compression mould
using processing temperature of 80 °C. The plate contained 85 wt-% of polyester resin and 15
wt-% of cellulose. The crosslinking was done at 150 °C for 2 minutes. The surface of the plate
was smooth and clear, in addition, the plate was hard and persistent.

10

Example 22.

Compression moulding with cup mould

To a methacrylated polyester resin according the Example 11 was blended 20 wt-% of
15   chopped glass fiber in a melt mixer at the temperature of 70 °C for 2 minute, 1 wt-% of
bis(tert-butylperoxyisopropyl)benzene (Perkadox 14) was added and the mixing was
continued for 1 minutes. Some of the resin mixture was put into Teflon cup mould and the
mould was put in the oven at 80 °C for 5 minutes. The other part of the mould was pressed on
top of the mould which was in the oven. The crosslinking was done by keeping the mould
20   system in the heating chamber at 160 °C 5 minutes, whereat a hard and smooth surfaced,
water and grease resistant cup was produced.

Example 23.

Gluing the steel plates

25

To an end-functionalised polyester resin according the Example 11 was blended 1 wt-% of
bis(tert-butylperoxyisopropyl)benzene (Perkadox 14) in a melt mixer at the temperature of 70
°C for 2 minute. The mixture was applied as a melt on the surface of the steel plate; the other
plate was pressed on the top of the melt resin. The crosslinking was performed in the heating
30   chamber, where the layer plate was held at 160 °C for 5 minutes.

Example 24

Redox crosslinking

A resin according to Example 10 was end-functionalised according to Example 11. To the methacrylated polyester resin was blended 1.1 wt-% of dibentsoyl peroxide and 2 wt-% of N,N-dimethyl-p-toluidine at room temperature. After 1.5 hours a crosslinked elastic and stiff polyester resin was produced.

Example 25.
Photocuring

To an end-functionalised polyester resin was added 2 wt-% of camphorquinone and 2 wt-% of N,N-dimethylaminoethylmethacrylate. The mixture was photocured by using a photoinitiator applying blue light for 40 seconds (wave length 400-500 nm) and a crosslinked, tough and stiff plastic alike material was obtained as a product.

Example 26.
Dispersion

25 wt-% of a polyester resin according to Example 11 with 1 wt-% of blended bis(tert-butylperoxyisopropyl)benzene (Perkadox 14) was blended in hot water by adding it gradually as a melt during vigorous mixing with the help of surfactant natriumdodecylsulphate. The mixing was continued for 2 minutes and the mixture was cooled down. A milky dispersion was obtained which remain stable. This dispersion was applied on the surface of paper. The paper was put in the heating chamber at 160 °C, where water evaporated and a thin crosslinked polymer film was produced on the paper surface.

Example 27.
Veneer

A polyester resin according to Example 11 was applied on the surface of veneer boards. Five boards were placed on top of each other and pressed against each other by compression mould at a temperature of 150 °C for 5 minutes. A multi-layered veneer-like plate was obtained.

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Claims

1. Essentially, a crosslinked polymer produced by a polycondensation from biodegradable or biomass based starting materials which essentially composes of

   a. structural units derived from hydroxy acid units or structural units derived from dicarboxylic acid units and diol units and

   b. possibly used functionalisation agent, which can be diol or multi-functional alcohol or diacid or multi-functional acid and

   c. possibly used unsaturated difunctional monomers and

   d. possibly used properties modifying monomer,
   characterized in that the end-groups are partly of entirely treated with acid or compound derived from acid or isocyanate compound or epoxy compound or multifunctional alcohol before crosslinking.

2. A polyester resin composition according to Claim 1, **characterized** in that it is composed at 0.1-99.8 mole-% of monomer units according to Claim 1a, 0.1-70 mole-% of unsaturated difunctional monomers according to Claim 1c, and 0.1-40 mole-% of polyol or polyacid monomers and 0-50 mole-% of modifying component 1d, preferably 60-97 mole-% hydroxy acid monomers and 0.5-15 mole-% polyol or polyacid monomers.

3. A polyester resin composition according to Claim 1, **characterized** in that its structural units derived from hydroxyl acid monomers compose of L-lactic acid monomer, D-lactic acid monomer or their mixtures.

4. A polyester resin according to Claims 1-3, **characterized** in that the hydroxyl acid monomers are composed of L-lactic acid monomers, D- lactic acid monomers or their mixtures and ε-caprolactone.

5. A polyester resin according to Claim 4, **characterized** in that the hydroxy acid part is composed of 99-1 mole-% of component A and 1-99 mole-% of component B

6. A polyester resin composition according to Claim 1, **characterized** in that the unsaturated difunctional monomers compose of itaconic acid, maleic acid, fumaric acid or their

anhydrides, or 1,4-butenediol, 1-propene-1,2-diol, 2-heptene-1,7-diol, 3-heptene-1,7-diol, 2-hexene-1,6-diol, 3-hexene-1,6-diol, 1-pentene-1,5-diol, 2-pentene-1,5-diol or betulin alias betulinol
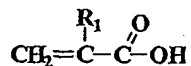
5   7. A polyester resin composition according to Claim 1, **characterized** in that polyol monomers are composed of 1,4-butanediol, glycol, propanediol, hexanediol, pentaerythritol, mannitol, glycerol or different polyglycerols or betulinol

8. A polyester resin composition according to Claim 1, **characterized** in that the polyacid
10   monomers are composed of 1,1,3-propane-tricarboxylic acid, 1,1,2-ethanecarboxylic acid or 1,2,3,4-cyclopentane-tetracarboxylic acid
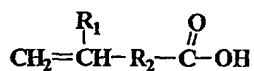
9. A polyester resin composition according to Claim 1, **characterized** in that the acid or compound derived from acid or isocyanate compound or epoxy compound or multifunctional
15   alcohol used in the treatment of end-groups contains entirely or partly unsaturated double bonds.

10. A polyester resin composition according to Claim 1, **characterized** in that the acid or compound derived from acid used in the treatment of end-groups is preferably organic
20   carboxylic acid, fatty acid, acid anhydride or acid chloride, octyl succinic anhydride, preferably methacrylic acid, methacrylic anhydride, itaconic acid, itaconic acid anhydride, linoliec acid, risinoliec acid, formic acid or acetic acid.

11. A polyester resin composition according to Claim 1, **characterized** in that the acid or unit
25   derived from acid in the treatment of end-groups is
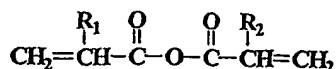
$$CH_2=\overset{\displaystyle R_1}{\underset{\displaystyle |}{C}}-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-OH$$

or

$$CH_2=CH-\overset{\displaystyle R_1}{\underset{\displaystyle |}{}}R_2-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-OH$$

30   or

$$CH_2=CH-\overset{\overset{\displaystyle R_1}{|}}{C}-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{\overset{\displaystyle R_2}{|}}{C}-CH=CH_2$$

or

$$CH_2=CH-R_2-\overset{\overset{\displaystyle R_1}{|}}{C}-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-R_3-\overset{\overset{\displaystyle R_4}{|}}{C}-CH=CH_2$$

5   or

$$CH_2=\overset{\overset{\displaystyle R_1}{|}}{C}-\overset{\overset{\displaystyle O}{\parallel}}{C}-Cl$$

or

10    $$CH_2=\overset{\overset{\displaystyle R_1}{|}}{C}-R_2-\overset{\overset{\displaystyle O}{\parallel}}{C}-Cl$$

or mixture of these where R_1, R_2, R_3 and R_4 are hydrogen, or some hydrocarbons or other chemical group.

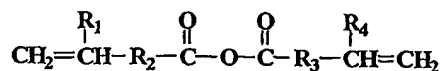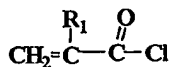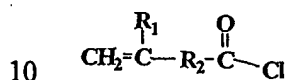15   12. A polyester resin composition according to Claim 1, **characterized** in that the treatment of end-groups with unsaturated compound enables and promotes the network formation in the crosslinking stage and improves some or all the following characteristics: crosslinking, mechanical strength, impact strength, modulus, water resistance, grease resistance, high temperature resistance and creep resistance.

20

13. A polyester resin composition according to Claim 1, **characterized** in that the components are mainly based on renewable raw materials, or biotechnically prepared.

14. A polyester resin composition according to Claim 1, **characterized** in that the structure of

25   the polyester resin is linear or branched before curing and crosslinked after curing.

15. A polyester resin composition according to Claim 1, **characterized** in that it can be crosslinked by using radical producing chemical compounds, which can be peroxides, azo compounds or redox compounds, or using heat, heat radiation, uv radiation, X-ray radiation,

30   gamma radiation or electron radiation.

16. A polyester resin composition according to Claim 1, **characterized** in that the other properties modifying monomer is ε-caprolactone, betulinol or itaconic acid.

5   17. A polyester resin according to Claim 1, **characterized** in that the crosslinked polymer has elastic or rubbery properties.

18. A polyester resin composition according to Claim 1, **characterized** in that it has been blended with reactive macromonomer, which improves the crosslinking.

10

19. A polyester resin composition according to Claim 1, **characterized** in that is can be used in well-known applications of crosslinkable polymers, such as curable thermoset, coating, binder, resin for hardener plastic, impregnation material, glue, paper coating, paper binder, dispersion, emulsion, solution, raw material for rubber, impact modifying blend component,
15   biomaterial, a coating or a blending component or an impregnated component for continuous or singular materials or products which comprise fibrous, porous, biomass based or inorganic materials, to provide them with water retention, barrier properties, elasticity, coherence or mechanical strength. It can be spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting and varnishing techniques in
20   dispersed or emulsified form, or that it can be moulded to objects.

20. A composition according to Claim 1, **characterized** in that the polyester resin prepared with the method can be spread as a coating, spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting techniques, or
25   that it can be moulded to objects, the material of which can be later crosslinked and that it can be processed with all processing methods of crosslinkable polymers and reinforced plastics, preferable such as coating, painting, roll coating, dispersion coating, curtain coating, extrusion, spray coating, compression moulding, prepreg techniques, RTM techniques, deep drawing from prepreg, winding pultrusion, rotational casting, blow molding, processing
30   methods of rubbers, it can be foamed and it can be made porous after which it is crosslinked to form a network structure.

21. A polyester resin composition according to Claim 1, **characterized** in that it is blended wiht fillers and reinforcement agents which are for example inorganic or organic compounds, preferable glass fibers, carbon fibers, polymer fibers, chalk, calcium carbonate, luster, TiO_2, carbon black, cellulose, paper mass, wood fibers, wood flour, wood groats, bark powder,

5   chips, lignin, betulin, flax fibers, starch, nanofillers such as montmorillonite, nanofibers, silica or microsilica, hydroxy apatite, bioactive glass and xerogels, glass flours, porosity producing porogens, one or many at the same time.

22. A polyester resin composition according to Claim 1, **characterized** in that from it can be

10   produce biodegradable packages, car components, house hold equipment, hygiene products, diapers, furniture, particle boards, veneer products, wood glue, paper, paper and cardboard products, disposable plates, paintings, colorants and glues, reinforced plastic products, toys, bottles, grease resistant packages, waste containers, waste bags, rubber products such as shoe soles, medical equipments, surgery equipments, tissue engineering materials and products,

15   drug delivery materials, implantable specimens and materials, electronic equipments, electronics components such as cell phone covers, foamed or porous specimens, not excluding other advantageous properties exploiting applications.

23.   A crosslinkable prepolymer produced by a polycondensation essentially from

20   biodegradable or biomass based starting materials, which essentially composes of

      a. structural units derived from hydroxy acid units or structural units derived from dicarboxylic acid units and diol units and

      b. possibly used functionalisation agent, which can be diol or multi-functional alcohol or diacid or multi-functional acid and

25   c. possibly used unsaturated difunctional monomers and

      d. possibly used of properties modifying monomer,

      characterized in that the end-groups are partly of entirely treated with acid or compound derived from acid or isocyanate compound or epoxy compound or multifunctional alcohol before crosslinking.

30

24. A polyester resin composition according to Claim 23, **characterized** in that it is composed at 0.1-99.8 mole-% of monomer units according to Claim 1a, 0.1-70 mole-% of unsaturated difunctional monomers according to Claim 1c, and 0.1-40 mole-% of polyol or

polyacid monomers and 0-50 mole-% of modifying component 1d, preferably 60-97 mole-%
hydroxy acid monomers and 0.5-1.5 mole-% polyol or polyacid monomers.

25. A polyester resin composition according to Claim 23, **characterized** in that its number
average molar mass is 200-50 000 g/mole, preferably 200-15 000 g/mole.

26. A polyester resin composition according to Claim 23, **characterized** in that its structural
units derived from compose of L-lactic acid monomer, D-lactic acid monomer or their
mixtures.

27. A polyester resin according to Claims 23-26, characterized in that the hydroxy acid
monomers compose of (A) L-lactic acid monomers, D-lactic acid monomers or their mixtures
and (B) ε-caprolactone.

28. A polyester resin composition according to Claim 27, **characterized** in that the hydroxy
acid part is composed of 99-1 mole-% of component A and 1-99 mole-% of component B.

29. A polyester resin composition according to Claim 23, **characterized** in that that the
unsaturated difunctional monomers compose of itaconic acid, maleic acid, fumaric acid or
their anhydrides, or 1,4-butenediol, 1-propene-1,2-diol, 2-heptene-1,7-diol, 3-heptene-1,7-
diol, 2-hexene-1,6-diol, 3-hexene-1,6-diol, 1-pentene-1,5-diol, 2-pentene-1,5-diol or betulin
alias betulinol

30. A polyester resin composition according to Claim 23, **characterized** in that polyol
monomers are composed of 1,4-butanediol, glycol, propanediol, hexanediol, pentaerythritol,
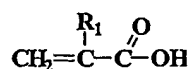mannitol, glycerol or different polyglycerols or betulinol

31. A polyester resin composition according to Claim 23, **characterized** in that the polyacid
monomers are composed of 1,1,3-propane-tricarboxylic acid, 1,1,2-ethanecarboxylic acid or
1,2,3,4-cyclopentane-tetracarboxylic acid.

32. A polyester resin composition according to Claim 23, **characterized** in that the acid or
compound derived from acid or isocyanate compound or epoxy compound or multifunctional
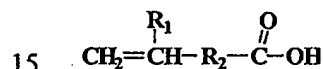
34

alcohol used in the treatment of end-groups contains entirely or partly unsaturated double bonds.

33. A polyester resin composition according to Claim 23, **characterized** in that the acid or compound derived from acid used in the treatment of end-groups is preferably organic carboxylic acid, fatty acid, acid anhydride or acid chloride, octyl succinic anhydride, preferably methacrylic acid, methacrylic anhydride, itaconic acid, itaconic acid anhydride, linoliec acid, risinoliec acid, formic acid or acetic acid.
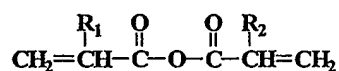
34. A polyester resin composition according to Claim 23, **characterized** in that the acid or unit derived from acid in the treatment of end-groups is form of:
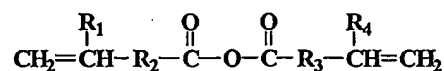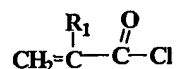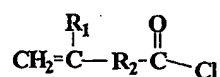
$$CH_2{=}\underset{\underset{R_1}{|}}{C}{-}\underset{\overset{O}{\|}}{C}{-}OH$$

or

$$CH_2{=}CH{-}R_2{-}\underset{\overset{O}{\|}}{C}{-}OH \quad (R_1)$$

or

$$CH_2{=}\underset{\underset{R_1}{|}}{CH}{-}\underset{\overset{O}{\|}}{C}{-}O{-}\underset{\overset{O}{\|}}{C}{-}\underset{\underset{R_2}{|}}{CH}{=}CH_2$$

or

$$CH_2{=}CH{-}\underset{\underset{R_1}{|}}{R_2}{-}\underset{\overset{O}{\|}}{C}{-}O{-}\underset{\overset{O}{\|}}{C}{-}R_3{-}\underset{\underset{R_4}{|}}{CH}{=}CH_2$$

or

$$CH_2{=}\underset{\underset{R_1}{|}}{C}{-}\underset{\overset{O}{\|}}{C}{-}Cl$$

or

$$CH_2{=}\underset{\underset{R_1}{|}}{C}{-}R_2{-}\underset{\overset{O}{\|}}{C}{-}Cl$$

or mixture of these where R_1, R_2, R_3 and R_4 are hydrogen, or some hydrocarbons or other chemical group.

35. A polyester resin composition according to Claim 23, **characterized** in that the treatment of end-groups with unsaturated compound enables and promotes the network formation in the crosslinking stage and improves some or all the following characteristics: crosslinking, mechanical strength, impact strength, modulus, water resistance, grease resistance, high temperature resistance and creep resistance.

36. A polyester resin composition according to Claim 23, **characterized** in that the components are mainly based on renewable raw materials, or biotechnically prepared.

37. A polyester resin composition according to Claim 23, **characterized** in that the structure of the polyester resin is linear or branched before curing and crosslinked after curing.

38. A polyester resin composition according to Claim 23, **characterized** in that it can be crosslinked by using radical producing chemical compounds, which can be peroxides, azo compounds or redox compounds, or using heat, heat radiation, uv radiation, X-ray radiation, gamma radiation or electron radiation.

39. A polyester resin composition according to Claim 23, **characterized** in that the other properties modifying monomer is ε-caprolactone, betulinol or itaconic acid.

40. A polyester resin according to Claim 23, **characterized** in that the crosslinked polymer has elastic or rubbery properties.

41. A polyester resin composition according to Claim 23, **characterized** in that it has been blended with reactive macromonomer, which improves the crosslinking.

42. A polyester resin composition according to Claim 23, **characterized** in that is can be used in well-known applications of crosslinkable polymers, such as curable thermoset, coating, binder, resin for reinforced plastic, impregnation material, glue, paper coating, paper binder, dispersion, emulsion, liquid, raw material for rubber, impact modifying blend component, biomaterial, a coating or a blending component or an impregnated component for continuous or singular materials or products which comprise fibrous, porous, biomass based or inorganic materials, to provide them with water retention, barrier properties, elasticity, coherence or

mechanical strength. It can be spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting and varnishing techniques in dispersed or emulsified form, or that it can be moulded to objects.

5   43. A composition according to Claim 23, **characterized** in that the polyester resin prepared with the method can be spread as a coating, spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting techniques, or that it can be moulded to objects, the material of which can be later crosslinked and that it can be processed with all processing methods of crosslinkable polymers and reinforced plastics,

10   preferable such as coating, painting, roll coating, dispersion coating, curtain coating, extrusion, spray coating, compression moulding, prepreg techniques, RTM techniques, deep drawing from prepreg, winding pultrusion, rotational casting, blow molding, processing methods of rubbers, it can be foamed and it can be made porous after which it is crosslinked to form a network structure.

15

44. A polyester resin composition according to Claim 23, **characterized** in that it is blended wiht fillers and reinforcement agents which are for example inorganic or organic compounds, preferable glass fibers, carbon fibers, polymer fibers, chalk, calcium carbonate, luster, TiO_2, carbon black, cellulose, paper mass, wood fibers, wood flour, wood groats, bark powder,

20   chips, lignin, betulin, flax fibers, starch, nanofillers such as montmorillonite, nanofibers, silica or microsilica, hydroxy apatite, bioactive glass and xerogels, glass flours, porosity producing porogens, one or many at the same time.

45. A polyester resin composition according to Claim 23, **characterized** in that from it can be

25   produce biodegradable packages, car components, house hold equipment, hygiene products, diapers, furniture, particle boards, veneer products, wood glue, paper, paper and cardboard products, disposable plates, paintings, colorants and glues, reinforced plastic products, toys, bottles, grease resistant packages, waste containers, waste bags, rubber products such as shoe soles, medical equipments, surgery equipments, tissue engineering materials and products,

30   drug delivery materials, implantable specimens and materials, electronic equipments, electronics components such as cell phone covers, foamed or porous specimens, not excluding other advantageous properties exploiting applications.

46. A method to produce crosslinkable polymer essentially based on biodegradable or biomass based materials and that is produced by polycondensation, which essentially composes of

    a. structural units derived from hydroxy acid units or structural units derived from

5   dicarboxylic acid units and diol units and

    b. possibly used functionalisation agent, which can be diol or multi-functional alcohol or diacid or multi-functional acid and

    c. possibly used unsaturated difunctional monomers and

    d. possibly used properties modifying monomer,

10 **characterized** in that the end-groups are partly of entirely treated with acid or compound derived from acid or isocyanate compound or epoxy compound or multifunctional alcohol before crosslinking.

47. A method according to Claim 46, **characterized** in that the prepolymer is produced

15 without reduced pressure or in reduced pressure, preferably at absolut pressure of 1 bar using elevated temperature, preferably 150-230°C

48. A method according to Claim 46, **characterized** in that the production is performed in any stirred vessel, thin film evaporator, batchwise or continuously or using cascade reactors

20 with solvent or without solvent, preferably without solvent.

49. A method according to Claim 46, **characterized** in that the crosslinking can be obtained by any radical producing method such as radical producing chemical compounds, which can be peroxides, azo compounds or redox compounds, or using heat, heat radiation, uv radiation,

25 X-ray radiation, gamma radiation or electron radiation.

50. A method according to Claim 46, **characterized** in that the crosslinking can be improved with reactive macromonomer.

30 51. A method according to Claim 46, **characterized** in that the network formation alias crosslinking happens in a mould, in a press, on a continuous line, deep drawing, a film layer, in an impregnated mass or product, filler mixture, in conjunction with a production process,

38

preferably such as pultrusion or winding, lamination procedure, gluing action, in conjunction with surgery operation or dental care or in a living tissue.

52. A method according to Claim 46, **characterized** in that the polyester resin prepared with
5   the method can be spread as a coating, spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting techniques, or that it can be moulded to objects, the material of which can be later crosslinked and that it can be processed with all processing methods of crosslinkable polymers and reinforced plastics, preferable such as coating, painting, roll coating, dispersion coating, curtain coating,
10   extrusion, spray coating, compression moulding, prepreg techniques, RTM techniques, deep drawing from prepreg, winding pultrusion, rotation casting, blow molding, processing methods of rubbers, it can be foamed and it can be made porous after which it is crosslinked to form a network structure.
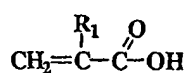
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AMENDED CLAIMS
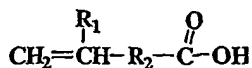### received by the International Bureau on 24 March 2006 (24.03.2006)

5   1. Essentially, a crosslinked polymer derived from biodegradable or biomass based starting
    materials **characterized in that** it composes of
    a. structural units derived from lactic acid or similar aliphatic hydroxy acids, or mixtures
        thereof, and
    b. pentaerytritol or a structurally similar functionalisation agent which is at least
10   trifunctional alcohol or carboxylic acid, and
    c. itaconic acid or a corresponding difunctional comonomer which has, in addition to
        reactive end groups, at least one reactive double bond in its molecules, and
    d. possibly used properties modifying comonomer which brings long flexible carbon-
        carbon chain segments between polymer chain linkages, for example ε-caprolactone,
15   and
    e. a carboxylic acid, a derivative of an organic acid or a monofunctional alcohol which
        has a reactive double bond or a reactive end-group in its molecules, and
    is prepared from said components stepwise first by polycondensing a monomer mixture being
    composed of 0,1 – 99,8 mole-% monomer units a, 0,1 – 40 mole-% functionalisation agent b,
20 0,1 – 70 mole-% unsaturated difunctional monomer c, and 0 – 50 mole-% properties
    modifying monomer d, and then by adding into the mixture 0,5 – 60 mole-% component e
    which reacts partly or entirely with the end-groups of the prepolymer before the final product
    is produced by crosslinking.

25 2. A crosslinked polymer according to Claim 1 **characterized in that** the hydroxy acid based
    part a is comprised of L-lactic acid, D-lactic acid, or mixtures thereof, and the possibly used
    properties modifying comonomer d is ε-caprolactone, of which a is used alone or in mixtures
    with d..

30 3. A crosslinked polymer according to Claim1 **characterized in that** the part of its structural
    units derived from hydroxy acid monomers and properties modifying monomer is composed
    of 100 – 50 mole-% component a and 0 – 50 mole-% component d.
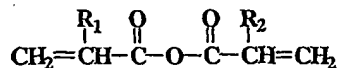
AMENDED SHEET (ARTICLE 19)

4. A crosslinked polymer according to Claim 1 **characterized in that** the unsaturated

difunctional monomers c comprise of itaconic acid, maleic acid, fumaric acid, or their

anhydrides, or 1,4-butenediol, 1-propene-1,2-diol, 2-heptene-1,7-diol, 3-heptene-1,7-diol, 2-

5   hexene-1,6-diol, 3-hexene-1,6-diol, 1-pentene-1,5-diol, 2-pentene-1,5-diol, or betulin alias

betulinol, or mixtures thereof.

5. A crosslinked polymer according to Claim 1 **characterized in that** the polyol monomers b

comprise of erytritol, pentaerythritol, mannitol, glycerol or different polyglycerols or

10   betulinol, each alone, or of mixtures thereof

6. A crosslinked polymer according to Claim 1 **characterized in that** the polyacid monomers

b comprise of 1,1,3-propanetricarboxylic acid, 1,1,2-ethanetricarboxylic acid, or 1,2,3,4-

cyclopentane-tetracarboxylic acid, or of mixtures thereof

15

7. A crosslinked polymer according to Claim 1 **characterized in that** the component e used

in the treatment of end-groups of the prepolymer before the crosslinking step is a carboxylic

acid, a derivative of an organic acid or a monofunctional alcohol which has a reactive carbon-

carbon double bond or a reactive end-group in its molecules.

20

8. A crosslinked polymer according to Claim 1 **characterized in that** the acid, or the

compound derived from an organic acid used in the treatment of end-groups of the

prepolymer is a carboxylic acid, a fatty acid, an organic acid anhydride or acid chloride,

preferably octyl succinic anhydride, methacrylic acid, methacrylic acid anhydride, itaconic

25   acid, itaconic acid anhydride, linolenic acid, risinolenic acid, or a mixture thereof.

9. A crosslinked polymer according to Claim 1 **characterized in that** the acid or the

compound e derived from an acid in the treatment of end-groups of the prepolymer is
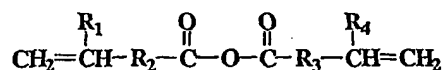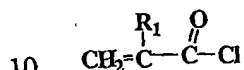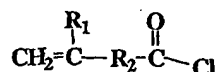
presented by a general formula

30

$$CH_2=\overset{R_1}{\underset{|}{C}}-\overset{O}{\underset{\|}{C}}-OH$$

or

$$CH_2=\overset{\overset{R_1}{|}}{CH}-R_2-\overset{\overset{O}{||}}{C}-OH$$

or

$$CH_2=\overset{\overset{R_1}{|}}{CH}-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-\overset{\overset{R_2}{|}}{CH}=CH_2$$

5   or

$$CH_2=\overset{\overset{R_1}{|}}{CH}-R_2-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-R_3-\overset{\overset{R_4}{|}}{CH}=CH_2$$

or

10    $$CH_2=\overset{\overset{R_1}{|}}{C}-\overset{\overset{O}{||}}{C}-Cl$$

or

$$CH_2=\overset{\overset{R_1}{|}}{C}-R_2-\overset{\overset{O}{||}}{C}-Cl$$

15   or a combination of these, where R_1, R_2, R_3 and R_4 are hydrogens, some saturated hydrocarbon chains, or other chemical groups.

10. A crosslinked polymer according to Claim 1 **characterized in that** the treatment of end-groups with unsaturated compound e enables and promotes the network formation in the final

20   crosslinking stage, and improves some, or all, the following product   characteristics: crosslinkability, mechanical strength, impact strength, Young's modulus, water resistance, grease resistance, high temperature resistance and creep resistance.

11. A crosslinked polymer according to Claim 1 **characterized in that** the components a, b,

25   c, and d are mainly based on renewable raw materials, or biotechnically prepared.

12. A crosslinked polymer according to Claim 1 **characterized in that** the molecular structure of the resin is branched, or star-shaped, before curing, and it forms a crosslinked network after curing.

13. A crosslinked polymer according to Claim 1 **characterized in that** it can be crosslinked by using radical producing chemical compounds which can be peroxides, azo compounds, or redox compounds, or using heat, heat radiation, ultraviolet radiation, X-ray radiation, gamma
5   radiation or electron radiation.

14. A crosslinked polymer according to Claim 1 **characterized in that** the possibly used properties modifying monomer d is ε-caprolactone, betulinol or itaconic acid.

10 15. A crosslinked polymer according to Claim 1 **characterized in that** the final crosslinked polymer is elastic, or it has rubbery properties.

16. A crosslinked polymer according to Claim 1 **characterized in that**, in addition to the treatment of end-groups of the prepolymer with the reactive compound e, it has been blended
15 with reactive comonomer c, or a reactive oligomeric macromonomer, which improves the crosslinking.

17. A crosslinked polymer according to Claim 1 **characterized in that** it can be used in many well-known applications of crosslinkable polymers, such as curable thermoset, coating,
20 binder, resin for reinforced plastic, impregnation material, glue, paper coating, paper binder, dispersion, emulsion, solution, raw material for rubber, impact modifying blend component, biomaterial, a coating or blending component, or an impregnated component for continuous web or piece materials or products which comprise fibrous, porous, biomass based or inorganic materials, to provide them with water retention, barrier properties, elasticity,
25 coherence or mechanical strength. It can be spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting and varnishing techniques in dispersed or emulsified form, or that it can be moulded to objects.

18. A crosslinked polymer according to Claim 1 **characterized in that** it can be processed
30 with all processing methods of crosslinkable polymers and reinforced plastics, preferably such as coating, painting, roll coating, dispersion coating, curtain coating, extrusion, spray coating, compression moulding, prepreg techniques, RTM techniques, deep drawing from prepreg, winding, pultrusion, rotational casting, blow molding, rubber processing; and it can be

AMENDED SHEET (ARTICLE 19)

foamed so that the prepolymer is first made porous after which it is crosslinked to form a network structure.

19. A crosslinked polymer according to Claim 1 **characterized in that** it is blended with various fillers and reinforcement agents which are, for example, inorganic or organic compounds, preferably glass fibers, carbon fibers, polymer fibers, chalk, calcium carbonate, kaolin, mica, alumininum hydroxide, calcium oxide, TiO_2, carbon black, cellulose, paper mass, wood fibers, wood flour, wood groats, bark powder, chips, lignin, betulin, flax fibers, starch, nanofillers such as montmorillonite, nanofibers, silica or microsilica, hydroxy apatite, bioactive glass and xerogels, glass flours, porosity producing porogens, alone or many at the same time.

20. A crosslinked polymer according to Claim 1 **characterized in that** it can be used as raw material for biodegradable packages, car components, household equipment, hygiene products, diapers, furniture, particle boards, veneer products, wood glue, paper, paper and cardboard products, disposable plates, paints, glues, reinforced plastics products, toys, bottles, grease resistant packages, waste containers, waste bags, rubber products such as shoe soles, medical equipments, surgery products, tissue engineering materials and products, drug delivery materials, implantable specimens and materials, electronic equipments, electronics components such as cell phone covers, foamed or porous objects, not excluding other possible applications exploiting the advantageous properties of the material.

21. A crosslinkable prepolymer produced from essentially biodegradable, or biomass based, starting materials **characterized in that** it composes of
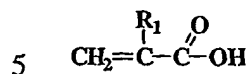
a. structural units derived from lactic acid or similar aliphatic hydroxy acid, or mixtures thereof, and

b. pentaerytritol or a structurally similar functionalisation agent which is at least trifunctional alcohol or carboxylic acid, and

c. itaconic acid or a corresponding unsaturated difunctional comonomer which has, in addition to reactive end-groups, at least one reactive double bond in its molecules, and

d. possibly used properties modifying comonomer which brings long flexible carbon-carbon chain segments between polymer chain linkages, for example ε–caprolactone, and

is prepared from said components by polycondensing a monomer mixture being composed of 0,1 – 99,8 mole-% monomer units a, 0,1 – 40 mole-% functionalisation agent b, 0,1 – 70 mole-% unsaturated difunctional monomer c, and 0 – 50 mole-% properties modifying monomer d, preferably containing 60 -97 mole-% structural units a derived from aliphatic hydroxy acids and 0,5 – 15 mole-% functionalisation agent b which is a polyol or .polyfunctional carboxylic acid.
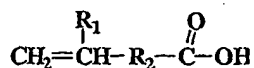
22. A prepolymer according to Claim 21 **characterized in that** its number average molar mass is 200 - 50 000 g/mole, preferably in the region of 200-15 000 g/mole.

23. A prepolymer according to Claim 21 **characterized in that** the hydroxy acid based part a is comprised of L-lactic acid, D-lactic acid, or mixtures thereof, and the possibly used properties modifying comonomer d is ε-caprolactone, of which a is used alone, or in mixtures with d.

24. A prepolymer according to Claim 21 **characterized in that** the part of its structural units derived from hydroxy acids and properties modifying monomer is composed of 100 - 50 mole-% of component a and 0 – 50 mole-% of component d.

25. A prepolymer according to Claim 21 **characterized in that** the unsaturated difunctional monomers c compose of itaconic acid, maleic acid, fumaric acid or their anhydrides, or 1,4-butenediol, 1-propene-1,2-diol, 2-heptene-1,7-diol, 3-heptene-1,7-diol, 2-hexene-1,6-diol, 3-hexene-1,6-diol, 1-pentene-1,5-diol, 2-pentene-1,5-diol or betulin alias betulinol, or mixtures thereof.

26. A prepolymer according to Claim 21 **characterized in that** polyol monomers b are composed of erytritol, pentaerythritol, mannitol, glycerol or different polyglycerols or betulinol, or of mixtures thereof.

27. A prepolymer according to Claim 21 **characterized in that** the polyacid monomers b are composed of 1,1,3-propanetricarboxylic acid, 1,1,2-ethanetricarboxylic acid or 1,2,3,4-cyclopentanetetracarboxylic acid, or of mixtures thereof.

28. A prepolymer according to Claim 21 **characterized in that** the possibly used properties modifying monomer d is ε-caprolactone, betulinol or itaconic acid

29. A prepolymer according to Claim 21 **characterized in that** the polymer crosslinked of it
5   is elastic, or it has rubbery properties

30. A prepolymer according to Claim 21 **characterized in that** its crosslinkability has been improved by blending with a reactive oligomeric macromonomer

10   31. A prepolymer according to Claim 21 **characterized in that** its components a, b, c, and d are mainly based on renewable raw materials, or biotechnically prepared

32. A prepolymer according to Claim 21 **characterized in that** its molecular structure is branched or star-shaped.
15

33. A prepolymer according to Claim 21 **characterized in that** the treatment of its end-groups with a compound carrying chemical unsaturation enables and promotes the network formation in the final crosslinking stage of the polymer, and improves some, or all, of the following characteristics: crosslinkability, mechanical strength, impact strength, Young's
20   modulus, water resistance, grease resistance, high temperature resistance and creep resistance.

34. A prepolymer according to Claim 21 **characterized in that** the acid or compound derived from acid or a monofunctional alcohol used in the treatment of its end-groups has a reactive carbon-carbon double bond or a reactive end-group in its molecules.
25

35. A prepolymer according to Claim 21 **characterized in that** the acid or the compound derived from acid used in the treatment of its end-groups is preferably a carboxylic acid, a fatty acid, an organic acid anhydride or acid chloride, or octyl succinic anhydride, and most preferably methacrylic acid, methacrylic anhydride, itaconic acid, itaconic acid anhydride,
30   linolenic acid, risinolenic acid, and some mixture of the mentioned compounds.
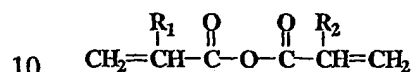
AMENDED SHEET (ARTICLE 19)

36. A prepolymer according to Claim 21 **characterized in that** the acid or the compound derived from an acid used in the treatment of its end-groups is presented by a general formula of the group:
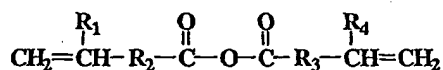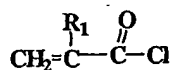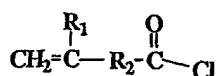
$$CH_2=C-C-OH$$

with R_1 and O groups

or

$$CH_2=CH-R_2-C-OH$$

with R_1 and O groups

or

$$CH_2=CH-C-O-C-CH=CH_2$$

with R_1, O, O, R_2 groups

or

$$CH_2=CH-R_2-C-O-C-R_3-CH=CH_2$$

with R_1, O, O, R_4 groups

or

$$CH_2=C-C-Cl$$

with R_1 and O groups

or

$$CH_2=C-R_2-C-Cl$$

with R_1 and O groups

where R_1, R_2, R_3 and R_4 are hydrogens, or some saturated hydrocarbon chains, or other chemical groups.

37. A prepolymer according to Claim 21 **characterized in that** it can be crosslinked by using radical producing chemical compounds, which can be peroxides, azo compounds or redox compounds, or using heat, heat radiation, ultraviolet radiation, X-ray radiation, gamma radiation or electron radiation.

38. A prepolymer according to Claim 21 **characterized in that** it can be used in well-known applications of crosslinkable polymers, such as curable thermoset, coating, binder, resin for reinforced plastic, impregnation material, glue, paper coating, paper binder, dispersion, emulsion, liquid, raw material for rubber, impact modifying blend component, biomaterial, a

5   coating or a blending component or an impregnated component for continuous web or piece materials or products which comprise fibrous, porous, biomass based or inorganic materials, to provide them with water retention, barrier properties, elasticity, coherence or mechanical strength. It can be spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting and varnishing techniques in dispersed

10   or emulsified form, or that it can be moulded to objects.

39. A prepolymer according to Claim 21 **characterized in that** the polymer resin prepared with the method can be spread as a coating, spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting techniques, or

15   that it can be moulded to objects, the material of which can be later crosslinked, and that it can be processed with all processing methods of crosslinkable polymers and reinforced plastics, preferable such as coating, painting, roll coating, dispersion coating, curtain coating, extrusion, spray coating, compression moulding, prepreg techniques, RTM techniques, deep drawing from prepreg, winding pultrusion, rotational casting, blow molding, processing

20   methods of rubbers, it can be foamed, and it can be made porous after which it is crosslinked to form a network structure.

40. A prepolymer according to Claim 21 **characterized in that** it is blended wiht fillers and reinforcement agents which are, for example, inorganic or organic compounds, preferable

25   glass fibers, carbon fibers, polymer fibers, chalk, calcium carbonate, kaolin, mica, gypsum, aluminum hydroxide, calcium oxide, TiO_2, carbon black, cellulose, paper mass, wood fibers, wood flour, wood groats, bark powder, chips, lignin, betulin, flax fibers, starch, nanofillers such as montmorillonite, nanofibers, silica or microsilica, hydroxy apatite, bioactive glass and xerogels, glass flours, porosity producing porogens, alone or many at the same time.

30

41. A prepolymer according to Claim 21 **characterized in that** it can be used as raw material for biodegradable packages, car components, house hold equipment, hygiene products, diapers, furniture, particle boards, veneer products, wood glue, paper, paper and cardboard

products, disposable plates, paintings, colorants and glues, reinforced plastic products, toys, bottles, grease resistant packages, waste containers, waste bags, rubber products such as shoe soles, medical equipments, surgery equipments, tissue engineering materials and products, drug delivery materials, implantable specimens and materials, electronic equipments, electronics components such as cell phone covers, foamed or porous objects, not excluding other applications exploiting the advantageous properties of the material.

42. A method to produce crosslinked polymer essentially based on biodegradable or biomass based materials **characterized in that** it is produced stepwise first by polycondensing a monomer mixture which essentially composes of:

a.   0,1 – 99,8 mole-% lactic acid or structural units derived from similar aliphatic hydroxy acids, and

b.   0,1 – 40 mole-% pentaerytritol or a corresponding functionalisation agent which is at least trifunctional alcohol or multi-functional carboxylic acid, and

c.   0,1 – 70 mole-% itaconic acid or corresponding unsaturated difunctional comonomer which has, in addition to reactive end-groups, at least one reactive double bond in its molecules, and

d.   0 – 50 mole-% possibly used   properties modifying monomer which brings long flexible carbon-carbon chain segments between polymer chain linkages,

and then possibly by adding into the mixture 0,5 – 60 mole-% a carboxylic acid, a derivative of an organic acid or a monofunctional alcohol which has a reactive carbon-carbon bond or a reactive end-group in its molecules, and by which the end-groups of the prepolymer are partly of entirely treated with before the final product is produced by crosslinking.
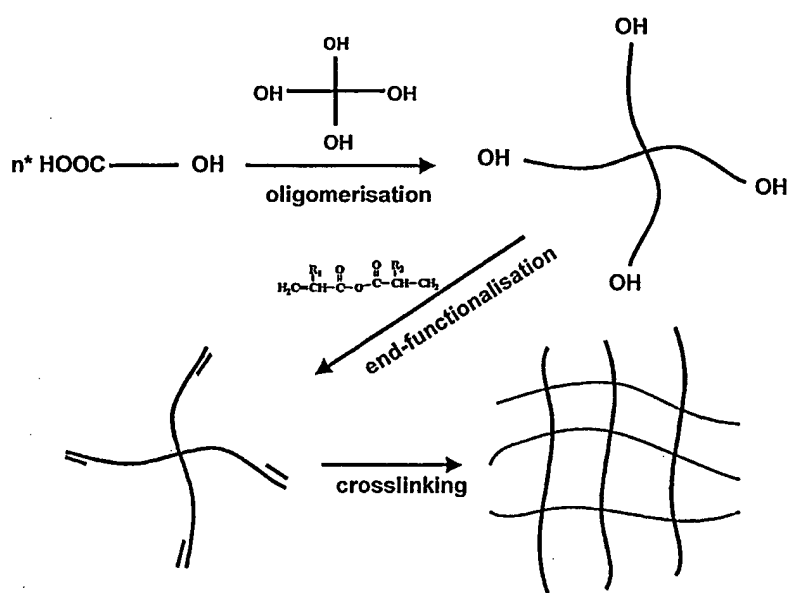
43. A method according to Claim 42 **characterized in that** the prepolymer is produced without reduced pressure or in reduced pressure, preferably at absolut pressure of 1 bar using an elevated temperature, preferably in the region of 150 - 230 °C.

44. A method according to Claim 42   **characterized in that** the preparation of the prepolymer, and the possible treatment of its end-groups with a compound carrying chemical. unsaturation in its molecules, is performed, batchwise or continuously, in any stirred vessel, thin film evaporator, or using cascade reactors with solvent or without solvent, preferably without solvent.

45. A method according to Claim 42 **characterized in that** the crosslinking of the final product can be obtained by any radical producing method, such as radical producing chemical compounds which can be peroxides, azo compounds or redox compounds, or using heat, heat radiation, ultraviolet radiation, X-ray radiation, gamma radiation or electron radiation.

46. A method according to Claim 42 **characterized in that** in addition to the treatment of end-groups of the prepolymer with a compound carrying chemical unsaturation in its molecules, the crosslinking can be improved by blending with a reactive oligomeric macromonomer.

47. A method according to Claim 42 **characterized in that** the network formation via crosslinking happens in a mould, in a press, on a continuous line, in deep drawing, in a film layer, in an impregnated mass or product, in a filler mixture, in conjunction with a production process, preferably such as pultrusion or winding, lamination procedure, gluing, in conjunction with surgery or dental care, or in a living tissue.

48. A method according to Claim 42 **characterized in that** the prepolymer prepared with the method can, either as itself or after treating the end-groups with a compound carrying unsaturation in its molecules, be spread as a coating, spread by a spraying technique as a liquid, spread by extrusion, pigment, hotmelt or wax coating techniques, spread by painting techniques, or in that it can be moulded to objects, the material of which can be later crosslinked to form a network-like material.

49. A method according to Claim 42 **characterized in that** the prepolymer prepared with the method can, either as itself or after treating the end-groups with a compound carrying unsaturation in its molecules, be processed by all processing methods for crosslinkable polymers and reinforced plastics, preferably by such as coating, painting, roll coating, dispersion coating, curtain coating, extrusion, spray coating, compression moulding, prepreg techniques, RTM techniques, deep drawing from prepreg, winding pultrusion, rotation casting, blow molding, rubber processing; and it can be foamed so that the prepolymer is first made porous after which it is crosslinked to form a network structure.

AMENDED SHEET (ARTICLE 19)

Statement under Article 19(1) PCT, relating to international application
PCT/FI2005/000471

The present invention discloses a new and widely applicable family of in a specific
and advantageous manner crosslinked thermosetting polymers of type polyester which
are obtained through a stepwise polymerization procedure. The polymerization
method utilized is also new because it is based on straight polycondensation of
aliphatic hyroxy acids, possibly with ε-caprolactone as comonomer, in mild
conditions, i.e. without reduced pressure or in reduced pressure and within the
temperature region of 150 – 230 °C, and then, if a specific, network-like structure is
preferred, partial or complete treatment of the prepolymer end-groups with an
unsaturated compound having a reactive double bond or a reactive end-group in its
molecules. However, the prepolymers obtained by the method are well crosslinkable
to form thermosetting polymeric products without any chemical treatment of their
reactive end-groups. So the whole polymerization procedure is flexible and well
usable to various applications of thermosetting biopolymers. In the prior art, the
polycondensation methods to produce corresponding crosslinkable polyesters have
based on reactions of dicarboxylic acids and diols, or ring-opening polymerization of
lactides or similar cyclic monomers aided by specific catalysts and requiring longish
reaction times and harsh conditions.

5   Figure 1.

A.	CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08F, C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

FI, DK, NO, SE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI, PAJ

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 7-133331 A (SHOWA HIGHPOLYMER) 23 May 1995 (23.05.1995) & World Patent Index [online] Derwent Publications, Ltd., Abstract Accession No. 1995-220803 [29]	1, 2, 6, 7, 9, 12-17, 19-25, 29, 30, 32, 35-40, 42-49, 51, 52 1-52
X Y	EP 1142596 A1 (UNIV GENT) 10 October 2001 (10.10.2001) claims 1, 16, 21, examples 1, 3, 9-10, page 4, lines 11-30, page 5, lines 18-44, page 6, line 37 - page 7, line 5	1, 3-5, 7, 9-23, 25-28, 30, 32-45 1-52
X Y	US 2003/0109647 A1 (LANG MEIDONG et al.) 12 June 2003 (12.06.2003) claims 1-6, examples 1-2, paragraphs [0012], [0021]	1, 3-5, 7, 9-23, 25-28, 30, 32-45 1-52
Y	WO 03/033563 A1 (FORTUM OYJ et al.) 24 April 2003 (24.04.2003)	1-52

☐	Further documents are listed in the continuation of Box C.	☒	See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 January 2006 (24.01.2006)	02 February 2006 (02.02.2006)

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EP 1142596 A1	10/10/2001	US 2003114552 A1	19/06/2003
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US 2003/0109647 A1	12/06/2003	WO 03011212 A2	13/02/2003
		JP 2004536929T T	09/12/2004
		EP 1411903 A2	28/04/2004
		CA 2450123 A1	13/02/2003
WO 03/033563 A1	24/04/2003	US 2005080223 A1	14/04/2005
		JP 2005505665T T	24/02/2005
		EP 1444285 A1	11/08/2004
		FI 20011999 A	16/04/2003

CLASSIFICATION OF SUBJECT MATTER

Int.Cl.
C08G 63/91 (2006.01)
C08F 290/14 (2006.01)